

TASK I SUMMARY REPORT

DEVELOPMENT OF A DISPERSION STRENGTHENED
NICKEL BASE ALLOY USING THE HIGH INTENSITY ARC PROCESS

by

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ABSTRACT

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A five component nickel base alloy, 20 Co-10 Mo-10W-balance Ni, containing 3 volume percent thoria as a dispersion strengthening oxide, was prepared successfully by the high intensity arc (Hierarc) process using a homogeneous consumable electrode. A homogeneous electrode formulation was developed which withstands the high thermal shock and vaporizes efficiently to yield a submicron oxide product of the desired composition. This oxide mixture is then reduced in hydrogen to yield the desired alloy powder.

Pressed and sintered specimens prepared from the hydrogen reduced sub-micron powder were examined electron microscopically and shown to contain ultrafine, uniformly dispersed, thorium oxide particles throughout the metal matrix.

author

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Vitro Laboratories

A. SUMMARY

The application of the high intensity arc process to the preparation of a multicomponent alloy powder containing a homogeneous submicron dispersion was successfully accomplished. The nominal composition of the alloy is 58 Ni, 20 Co, 10 Mo, 10 W and 2 ZrO₂ (or 3 ThO₂).

The major effort was devoted to the development of an electrode composition which:

1. is sufficiently strong to withstand the very high thermal shock during vaporization,
2. overcomes the inherent vaporization problems encountered when combining two groups of metals, namely Ni-Co and Mo-W, having widely different vaporization characteristics,
3. permits vaporization of the dispersion oxide to submicron particles homogeneously dispersed in the oxide fume product,
4. provides the desired composition of the final alloy.

In the development of high strength electrodes for vaporization, it was necessary to use a high sulfur bearing binder and carbon. A method was developed to reduce residual sulfur in the condensed fume product to less than 30 ppm without disturbing the particle size and homogeneity of the dispersed phase.

Electron microscopic evaluation of pressed and sintered specimens revealed that the high intensity arc process did not provide submicron particles from ZrO₂ in this alloy system, a phenomenon which is not completely understood at present. The utilization of ThO₂, however, provided

a very homogeneously dispersed oxide phase having an average particle size of 0.1 micron and an average interparticle spacing of less than 1.0 micron.

The studies of Task I have demonstrated that the high intensity arc process can be applied to the preparation of a multicomponent alloy powder containing a submicron dispersion which is uniformly distributed in the alloy matrix.

B. INTRODUCTION

The demand for iron, nickel and cobalt base alloys to withstand the temperature and stress regimes of future jet engine and space applications is becoming increasingly critical. Earlier emphasis was placed on the development of Fe, Ni, and Co-based alloys in which the high temperature strength is developed by utilizing solid solution and precipitation strengthening mechanisms. Unfortunately, increased operating temperatures and extended service requirements have exceeded the strengthening capabilities of these mechanisms since their effects are temperature dependent. Consequently, other strengthening methods must be pursued to realize the strengths required for advanced applications.

The most promising approach for achieving improved high temperature strengths is the utilization of the dispersion strengthening mechanisms where insoluble, hard, ultrafine particles are uniformly incorporated in a metal matrix. Although this type of strengthening is not new, it has not been utilized to a great extent due to the difficulty inherent in the preparation of ultrafine dispersion particles and the incorporation of these particles into a metal matrix in a completely random and homogeneous manner. Previous attempts to achieve good dispersions have been made by mechanical mixing of individual powders, co-precipitation and selective reduction, vapor deposition and reduction, and other methods.

Progress in the dispersion strengthening of metals has advanced to the stage where two alloys are commercially available, i.e. SAP aluminum and TD nickel. The development of TD nickel has demonstrated the feasibility of producing an alloy having high temperature strength capabilities in excess of the best cast or wrought processed alloy.

The purpose of this investigation, then, is to further develop a specific method, namely, the high intensity arc (Hierarc) process, for the preparation of a superalloy metal powder containing a dispersion meeting the requirements of particle size and distribution, and ultimately, to prepare sufficient material for stress rupture testing. The overall objective of this program is to develop and evaluate nickel base alloys, dispersion strengthened by thoria or zirconia, with the goal of producing a material having a 3000 hour stress rupture strength of 15,000 psi at 2000°F.

The high intensity arc process provides the following advantages in the preparation of complex alloys containing a dispersed phase:

1. Dispersion particles less than 1000 angstroms in diameter can be readily achieved.
2. Homogeneous distribution of dispersion particles is accomplished.
3. Any alloy composition whose oxides can be hydrogen reduced can be prepared by this method.
4. The basic method is simple.

A matrix composition of 20 Co, 10 Mo, 10 W, balance Ni and 3 to 8 volume percent dispersion of zirconia or thoria were selected for this study for the following reasons:

1. To provide a high strength solid solution alloy in which the dispersed phase can be fully evaluated without influence of secondary reactions.
2. To provide a very stable dispersed phase for further strengthening.
3. To demonstrate the merits of the Hierarc process in a complex system.

This report relates to the efforts of Task I in which the objective was to develop the Hierarc process for the preparation of a complex alloy powder and to demonstrate the capability of the process to provide an ultrafine, randomly dispersed phase of zirconia or thoria in the selected alloy matrix.

C. PROCESS DESCRIPTION AND PROCEDURE

1. Electrode Preparation

The basic premise of the high intensity arc process is the preparation of a submicron oxide by the vaporization of an electrode and the condensation and collection of the resulting oxide particles.

The approach selected to prepare submicron oxides was the homogeneous electrode technique. In this method, all of the alloying constituents, as metal or oxide powders, or combinations of the two, are thoroughly mixed with carbon and an organic binder, extruded, and baked to provide an electrically conductive electrode having sufficient strength to withstand the high thermal stresses encountered during arcing. The constitution of the electrode varies, particularly in the carbon content, because of the wide variation in the vaporization characteristics of different materials.

In this program, homogeneous electrodes were prepared using nickel and cobalt metal powders and oxides of tungsten, molybdenum and zirconium. Because of the significant differences in the vapor pressure-temperature relationships of the Ni-Co and Mo-W groups, it became necessary not only to develop electrodes having adequate strength but also electrode compositions having satisfactory overall vaporization characteristics.

The types of raw materials are dictated to a large extent by purity, availability, particle size and density. Generally, irregularly shaped, high density, minus 200 mesh powders are desirable for the preparation of electrodes. The purity level of the raw materials is important, particularly with regard to the carbon. Certain impurities in carbon will carry over into the product, and the higher the carbon content of the electrode, the greater the concentration of impurity in the product. Consequently, low ash contents are necessary. Lists of the raw materials used and their chemical analyses are given in Appendix A.

Appropriate amounts of -200 mesh nickel and cobalt metal powders and molybdenum, tungsten, and zirconium oxide powders are mixed in a Lancaster Countercurrent Batch Mixer with the carbon and binder until the mix is thoroughly blended and wetted. The mix is then extruded to 3/4" diameter electrodes approximately 36" in length and baked in a Harper Globar heated box type furnace. The heating cycle is programmed to 100°C per hour to 900°C with a 4 hour hold at temperature. The electrodes are

furnace cooled to below 200°C before removing them. Figures 1, 2, 3 and 4 show photographs of the mixer, extrusion press, baking furnace, and typical electrodes produced by this procedure.

2. Arc Vaporization (Hierarc) Process

The Hierarc Process features a high intensity electric arc as the energy source. The process material is incorporated into the anode, vaporized, and collected by condensation of the effluent vapors. One of the most important features of the high intensity arc is that the material to be vaporized is incorporated into the arc anode and all the constituents vaporized simultaneously. This permits direct application of a major fraction of the arc energy to the process material, thus achieving highly efficient energy transfer. When the high intensity mode of arc operation is used, the anode material is rapidly vaporized in the form of a plasma of ionized gas with a peak temperature of approximately 7000°C. The electrode is rotated which permits uniform burning at the anode face, and the arc gap is maintained by an electrically driven feed which is manually controlled. The graphite cathodes are fed in the same manner since these too are consumed due to the high temperatures generated.

The anode feed rates, which are governed by the rate of vaporization, vary depending upon the carbon content of the electrode and the power required for vaporization; the less the carbon content of the electrode and/or the higher the power, the greater the rate of vaporization. Because of the different vaporization modes of the materials used in this program, the maximum power level available, 40 kw, was used to vaporize all of the electrodes processed.

As soon as the plasma cools below the dew point, rapid condensation occurs in the form of extremely fine particles. This fine state of subdivision is due to the high density of positive ions and free electrons which present nucleation sites for a large number of individual particles and to the large temperature gradient along the plasma which permits rapid cooling of these particles so that they have little time to grow.

The vaporization of the homogeneous electrode (covaporization) provides a completely homogeneous mixture of all the electrode constituents and this homogeneity persists upon condensation of the plasma. Control of particle size can be maintained by quenching the plasma with an air jet. Fume particle sizes from 100-500 angstroms are readily achieved. Figures 5

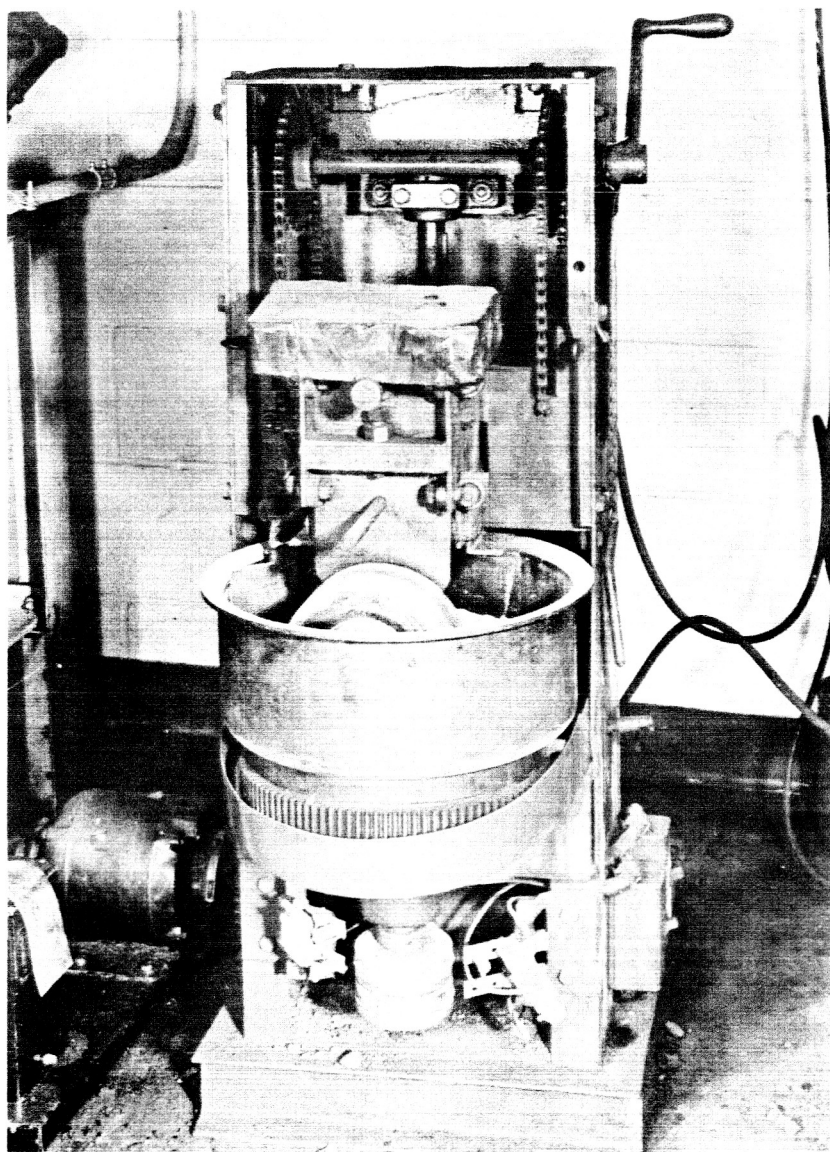


FIGURE 1
MIXER

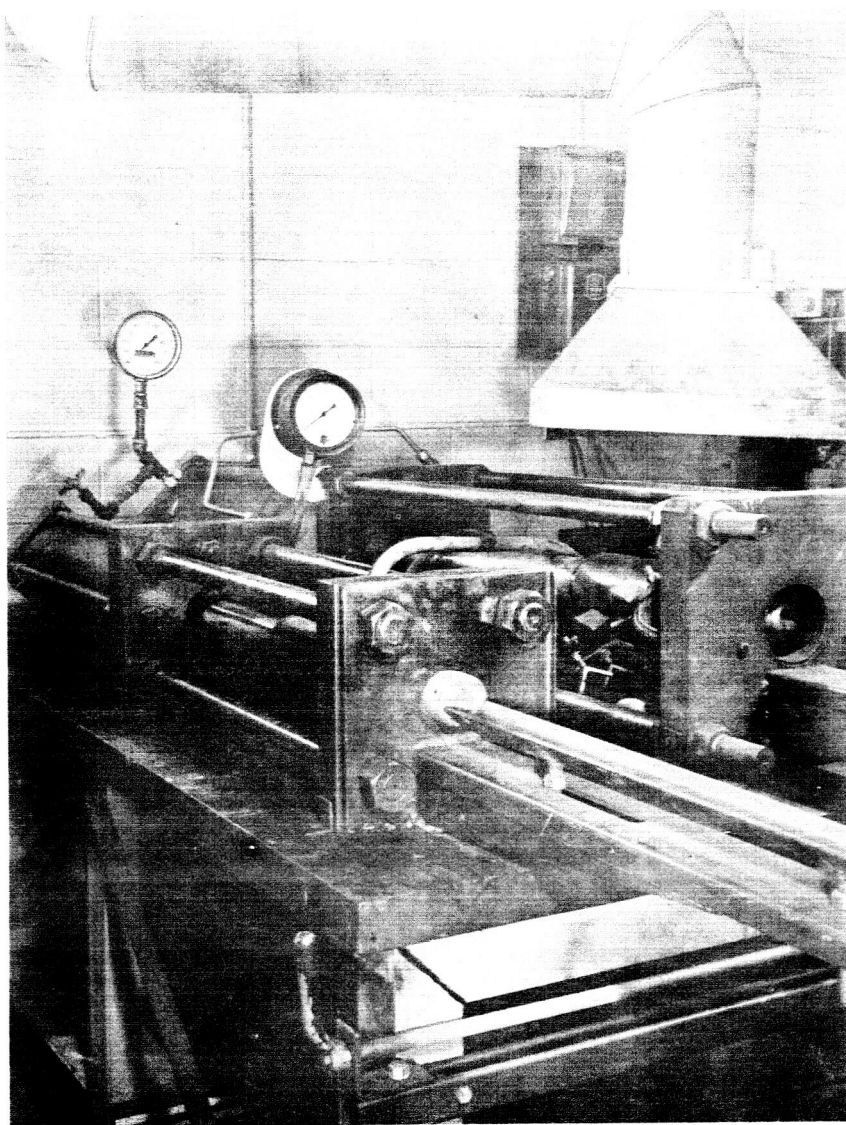


FIGURE 2
EXTRUSION PRESS

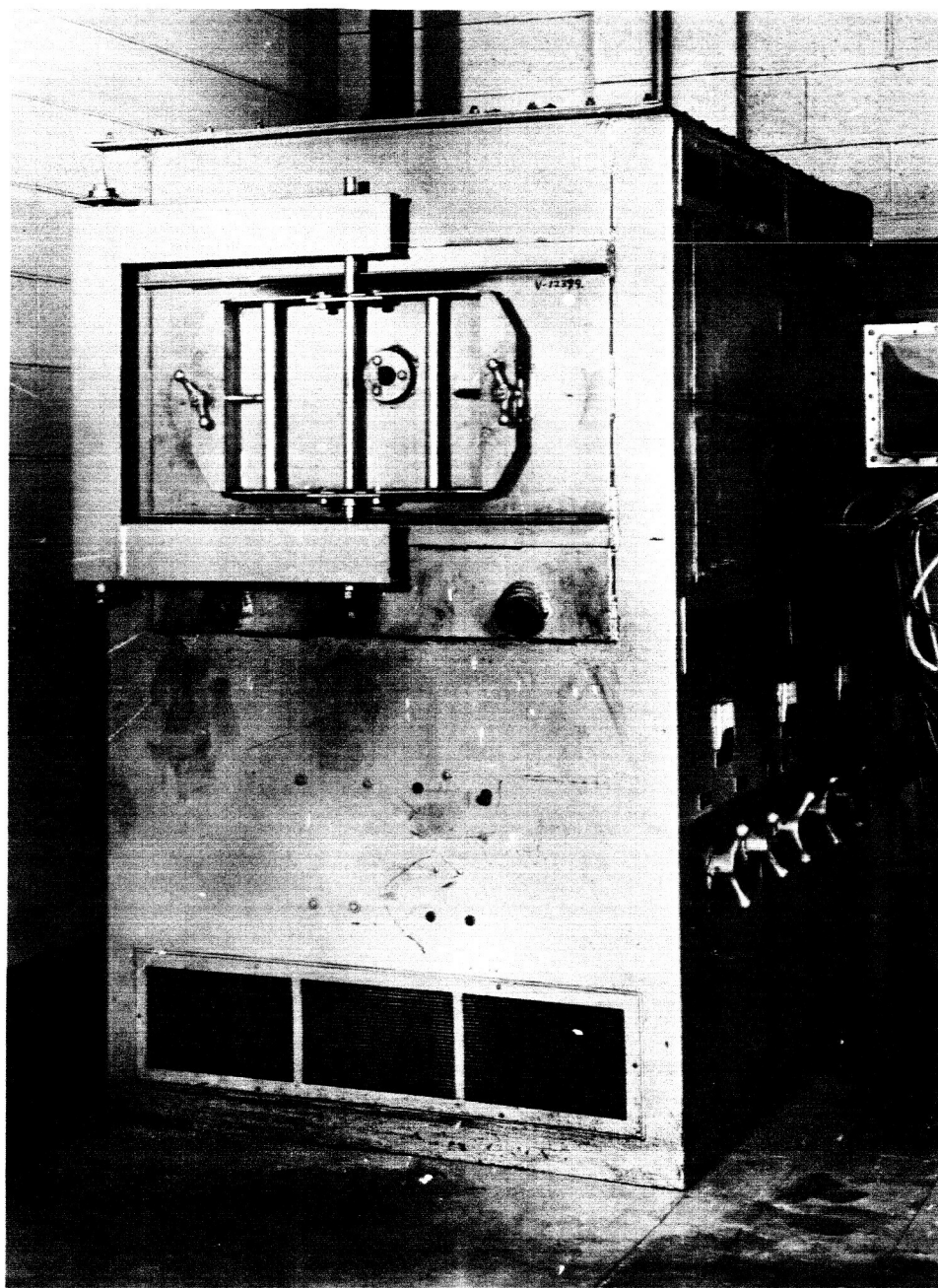


FIGURE 3
HARPER FURNACE FOR BAKING ELECTRODES

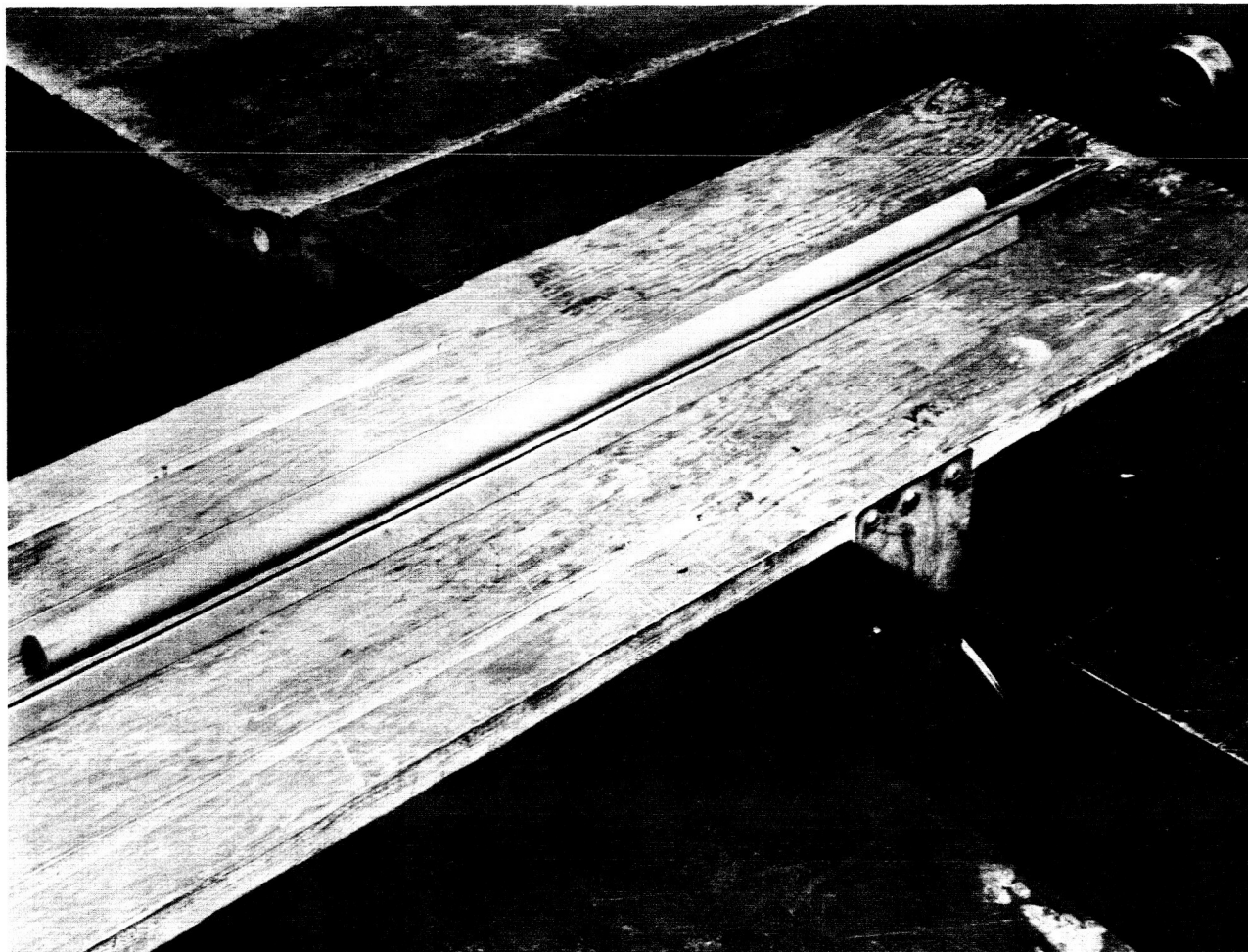


FIGURE 4
TYPICAL ELECTRODES

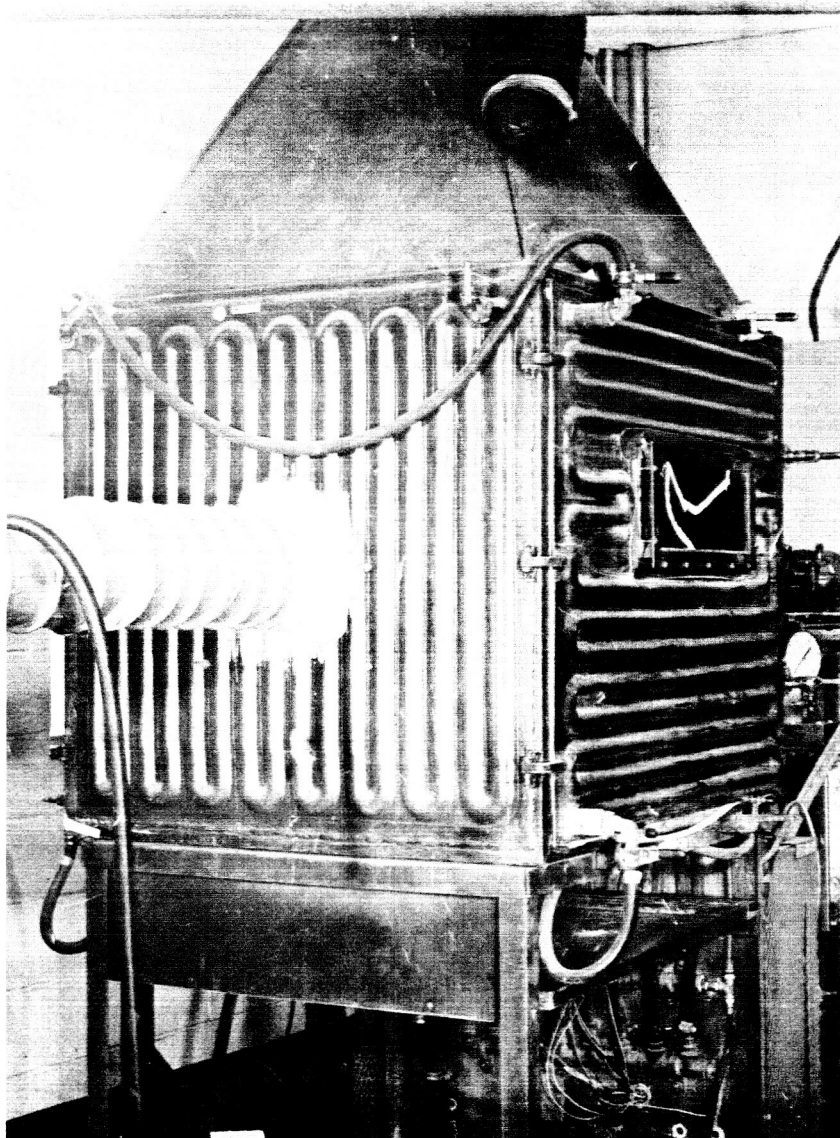


FIGURE 5
OVERALL ARC CHAMBER

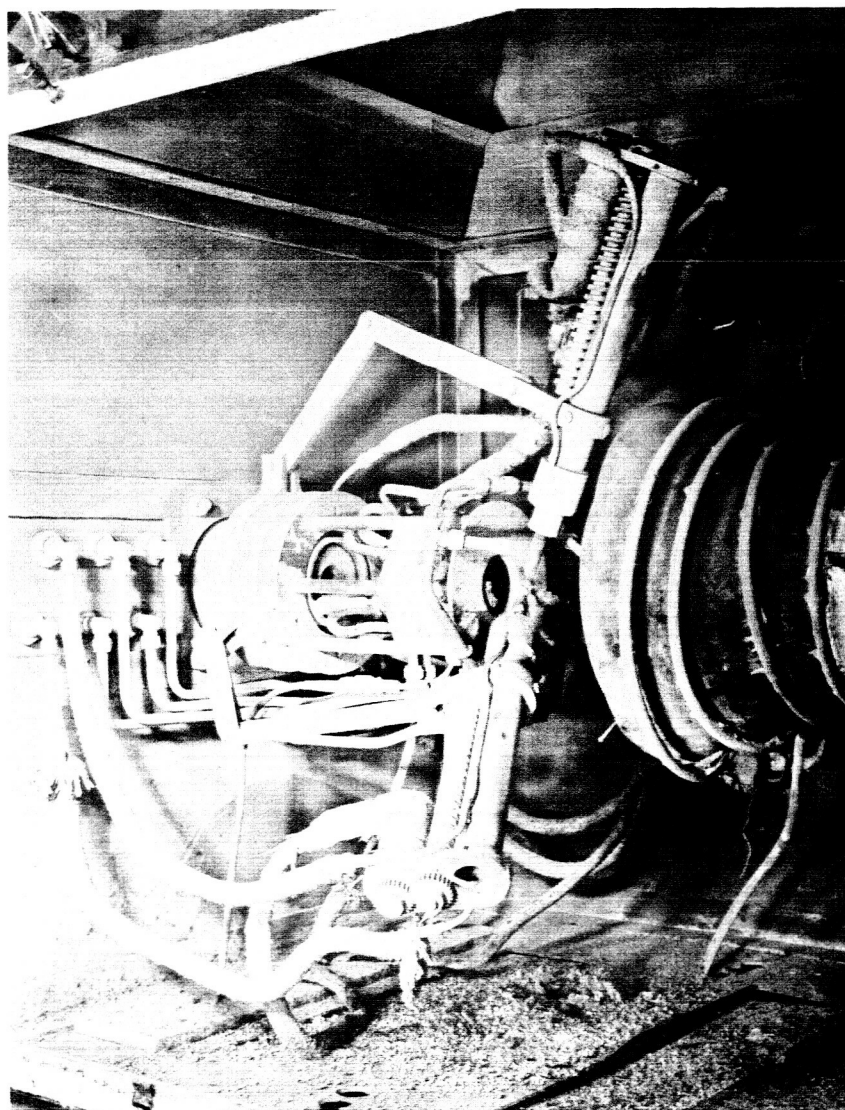


FIGURE 6
VAPORIZATION HEAD

and 6 are photographs of the arc chamber and the anode-cathode mechanisms, respectively. Figure 7 is a schematic of the arc operation.

The condensed fume is exhausted from the chamber by a high velocity air stream created by an exhaust blower on the discharge side of the bag collector. After leaving the chamber, the condensed fume passes through several cyclone collectors and is finally collected in a reverse jet bag collector as agglomerates held together electrostatically. The fume is collected in the container at the bottom of the bag collector shown in Figure 8. The submicron fume product contains all of the alloy constituents homogeneously blended by vapor phase mixing.

3. Reduction

The reduction of the submicron alloy oxide fume is carried out under a hydrogen atmosphere in a conventional batch type Inconel retort containing 5 trays in a Hayes box type furnace. The retort and its carriage are so designed that the reduced powder can be discharged into an argon atmosphere receptacle which can be detached and taken into an argon atmosphere drybox. The maximum capacity of the retort is approximately 1500 grams of oxide fume yielding about 1100 grams of reduced metal powder per charge.

The reduction of evaluation specimens is carried out in a 2" diameter Inconel tube furnace which is attached to the drybox. Reduced specimens are taken directly into the drybox under an argon atmosphere. Approximately 10 grams of oxide can be reduced per charge in this furnace.

The reduction conditions of time, temperature, hydrogen flow rate, depth of powder bed, etc., are dictated by the properties desired in the reduced metal powders. The cycle utilized for the alloy powder for this program was: ambient to 650°C in 15 hours; hold at 750°C for 3 hours including the 15 minutes required for heating from 650° to 750°C; then cool. The hydrogen flow rate was approximately 50 cu. ft./hr., and the depth of the oxide powder bed was maintained at 1/4". This cycle is considerably longer than that necessary, but was established as a matter of convenience since a shorter cycle could not be effected with this equipment within a normal working day.

The cycle utilized in the small tube retort is a 1 hour hold at 800°C after reaching temperature in approximately 1 hour.

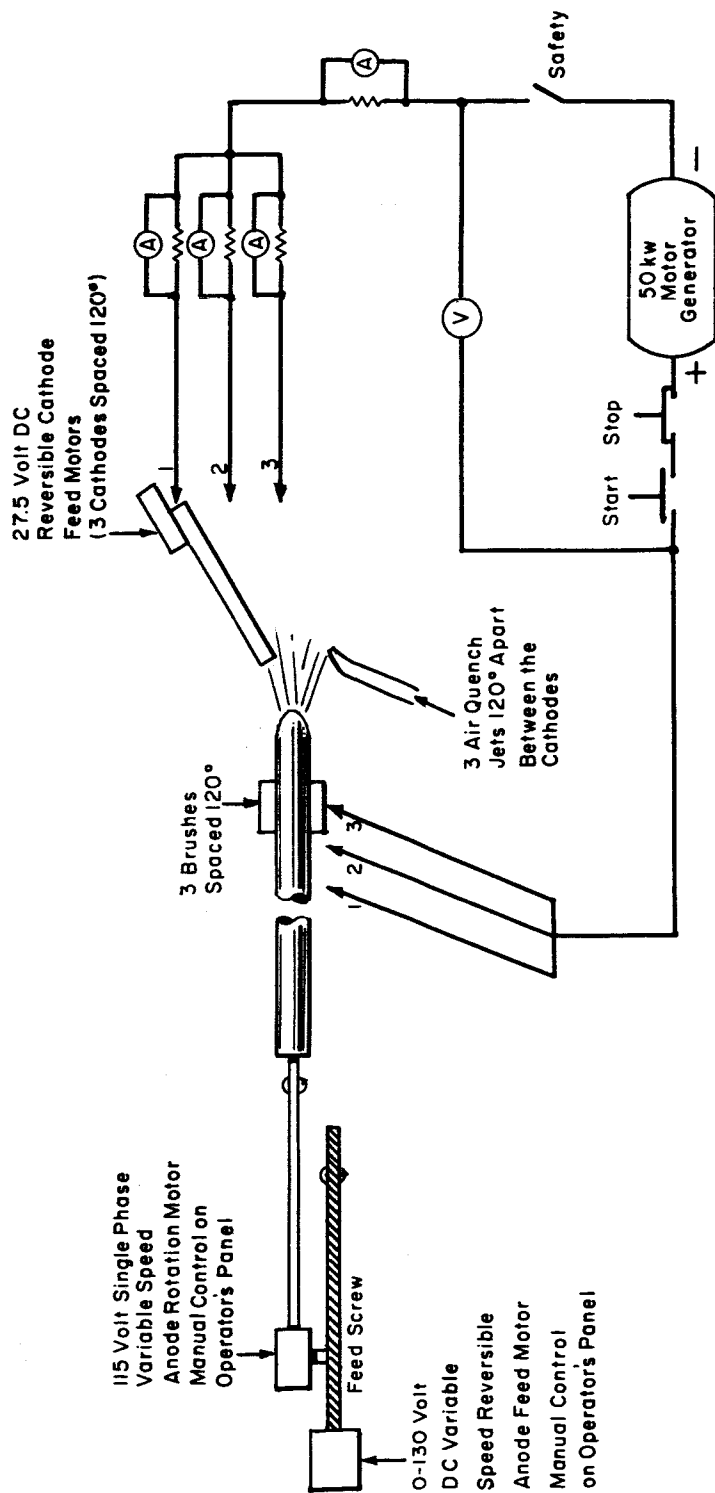


FIGURE 7
SCHEMATIC OF THE ARC SYSTEM

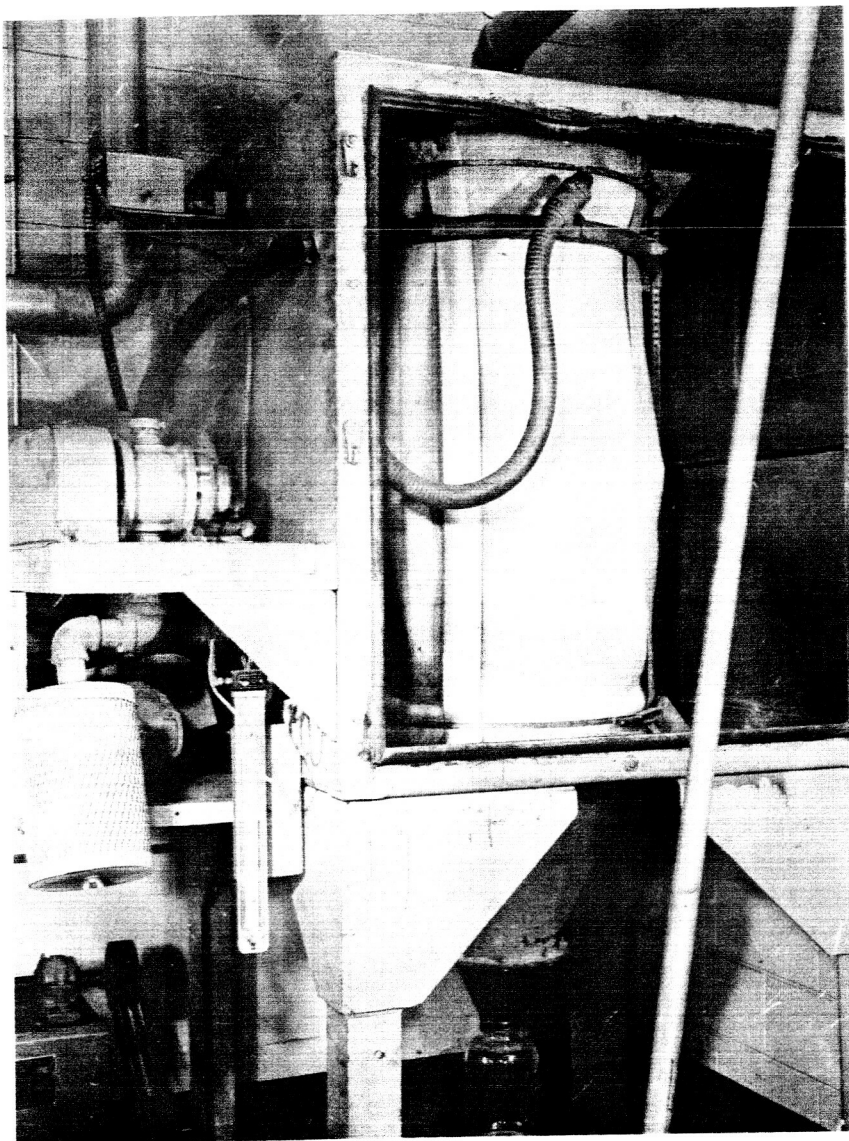


FIGURE 8
FUME COLLECTOR

Figures 9 and 10 show the reduction retort and the drybox with the small reduction tube, respectively. Figure 11 shows a flow chart of the over-all process for making metal powders by this process.

4. Pressing and Sintering

Metal powders were precompacted in a Carver press either in the drybox under an inert atmosphere or on the bench in air, bagged, evacuated, and isostatically pressed to the desired load. After stripping from the bag, the compacted specimens are sintered in hydrogen in a Globar type alundum tube furnace, or in a Model 1064 Brew vacuum furnace for the times and temperatures desired.

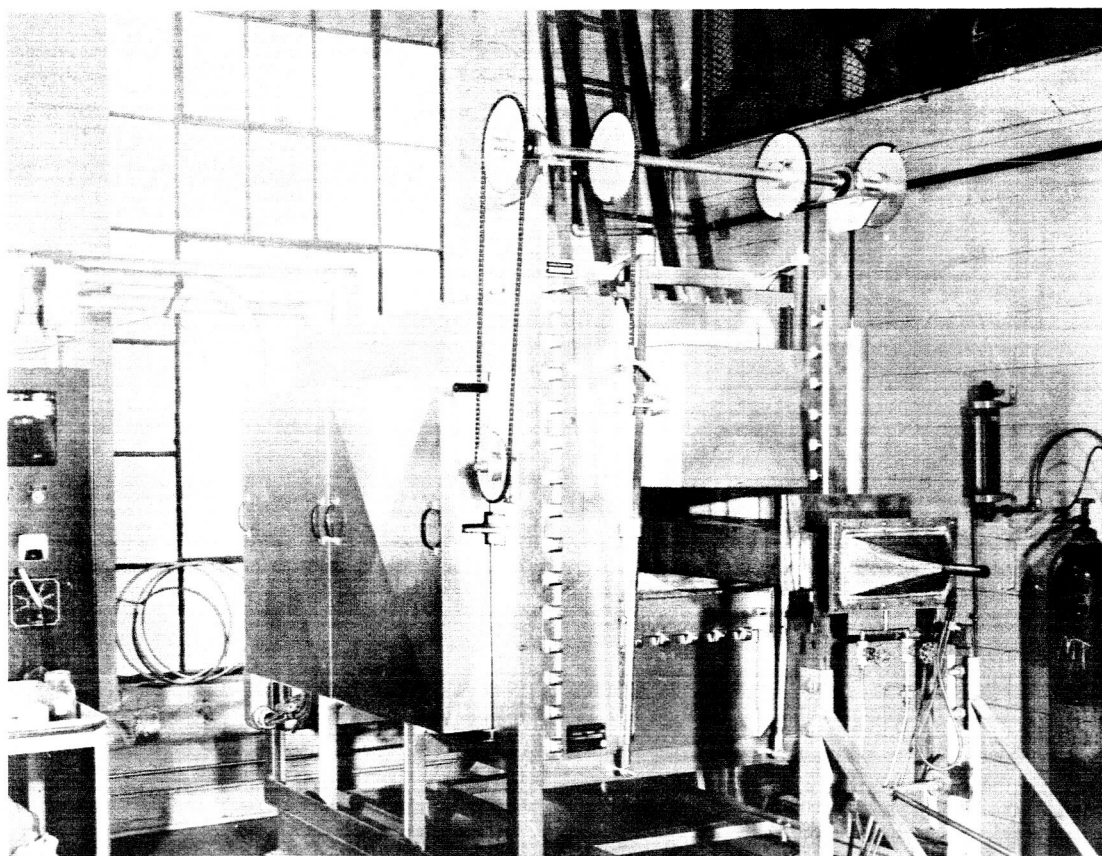


FIGURE 9
HYDROGEN REDUCTION RETORT
AND HAYES FURNACE

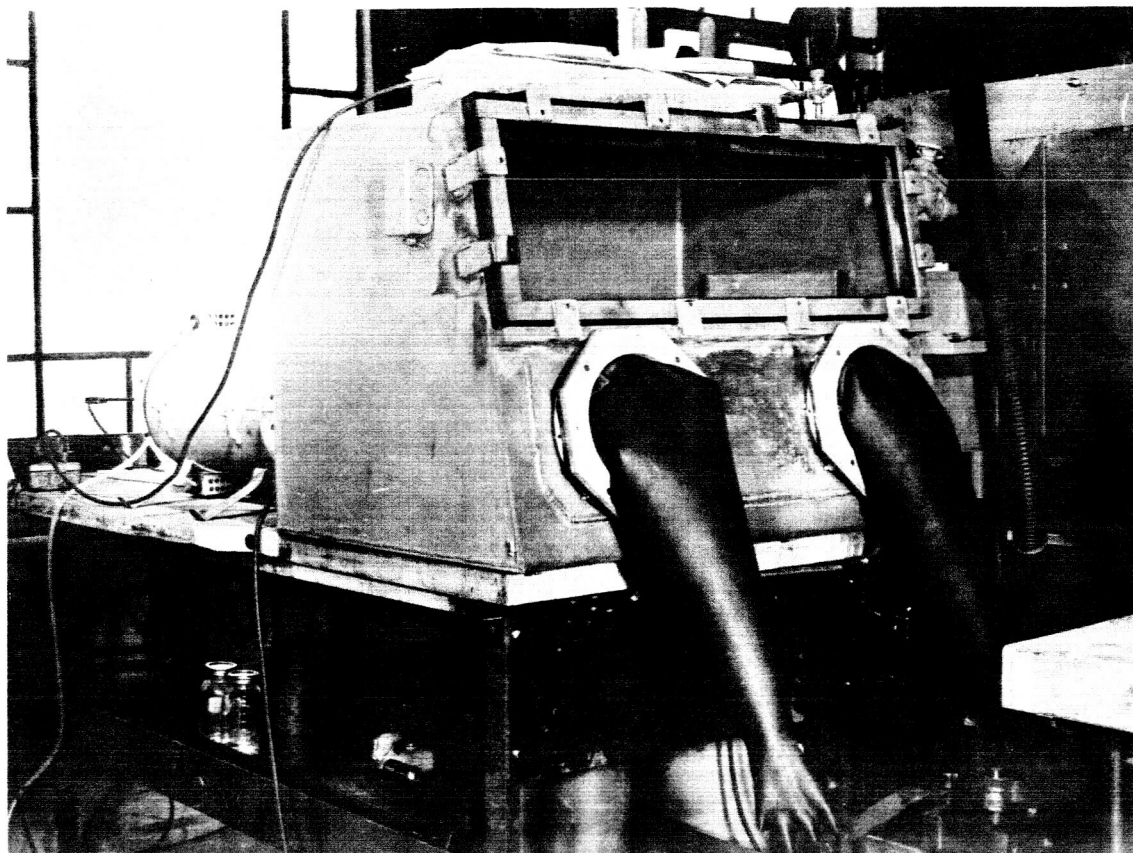


FIGURE 10
DRY BOX WITH TUBE REDUCTION RETORT

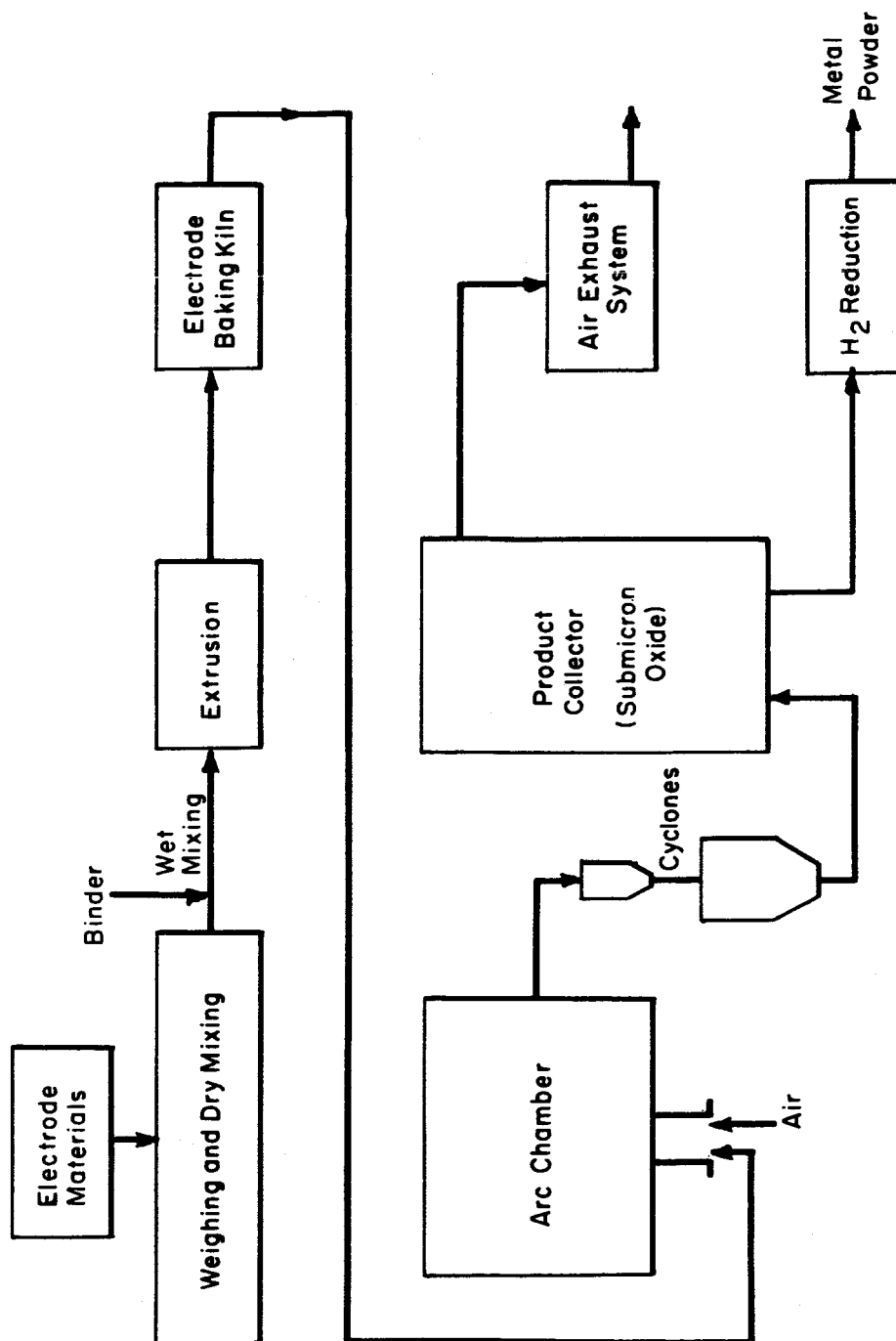


FIGURE 11
FLOW CHART FOR METAL PREPARATION
BY THE ARC PROCESS

D. EXPERIMENTAL AND ANALYTICAL RESULTS

1. Electrode Preparation and Arc Vaporization

The major effort of Task I was devoted to the development of an electrode formulation which provides an electrode having adequate strength and vaporization characteristics and desired purity levels in the product. Many problems arose in the selection of materials, particularly carbon, from the standpoint of purity and the ultimate ability to fabricate strong electrodes for vaporization. In addition, the two basic groups of elements, Ni-Co and Mo-W, which have widely different vaporization characteristics had to be incorporated into a homogeneous electrode in the proper ratio and with the proper carbon content to fulfill the above requirements of vaporization and strength, and yield a high purity oxide fume of the desired composition.

Because of the different vaporization modes of the two groups of materials, the Mo-W group does not vaporize as effectively as the Ni-Co group when combined into a homogeneous electrode. Furthermore, it appears that the Ni-Co group promotes reduction of $\text{MoO}_3\text{-WO}_3$ at the arc-anode interface forming molten drops of Mo-W metal which do not vaporize sufficiently rapidly and ultimately drop to the bottom of the chamber. Each of these groups, however, will vaporize very readily when separated.

In the initial attempts to improve the vaporization characteristics of the homogeneous electrode, carbon contents between 5 and 50 percent were studied. Table 1 lists some typical analytical results of electrode composition versus fume product composition from electrodes made with varying carbon contents.

Several runs in Table 1 are listed as two-step electrode fabrication. In the two-step method, one or more of the constituents is premixed with the binder, and cured and crushed prior to being mixed with the remainder of the mix. This method frequently improves electrode strength and burning characteristics. No improvements in vaporization were realized in this system within the limited studies made. In addition to poor and inconsistent electrode strengths, considerable melting and dripping occurred at the anode face during vaporization with electrodes containing low carbon contents. Electrodes containing up to 10% carbon dripped profusely and burned so rapidly that the maximum feed rate of the electrode was inadequate to maintain a continuous arc. Electrodes containing between 10 and 30% carbon dripped and ejected fine shot; the dripping decreased with increasing carbon content; and electrodes containing 30 to 50% carbon ejected fine shot

TABLE 1

CHEMICAL COMPOSITION OF ELECTRODE
AND FUME PRODUCT

Run No.	20	21	22	23(1)	24	25(2)	31	32(3)
EL								
EC	48.7(4)	49.8	48.1	46.6	34.1	77	48.2	52
ET	--	--	--	--	12.0	--	--	--
ER	21.2	20.6	21.2	22.1	18.6	10	21.4	23
OR	22.9	22.4	23.0	23.8	21.8	10	23.1	25
OD	7.2	7.1	7.2	7.5	14.3	3	7.3	--
OE	4.7	4.3	7.6	10.6	1.1	5	50	5
Carbon Equiv.								
P(5)								
RO	74	84.5	86	93.5	57.3		73	54.3
OD	--	--	--	--	11.0	Not	--	--
UC	12.9	5.1	8.9	4.5	7.8	Analyzed	11.8	17.6
CT	12.4	8.1	3.8	1.54	20.2		13.1	24.2
	1.68	2.06	1.28	.52	3.8		2.1	3.9

Runs 25 through 30 not analyzed due to poor burning or weak electrodes.

- (1) Two-step procedure for MoO_3 and WO_3 .
 (2) Two-step procedure for NiO , MoO_3 , WO_3 , and ZrO_2 .
 (3) Two-step procedure for Ni only.
 (4) All values weight percent.
 (5) Analysis on oxide calculated to reduced metal equivalent.

entirely. The electrodes containing 50% carbon appeared to have the best overall vaporization characteristics but the amount of oxide fume product produced per unit weight of electrode is very low due to the high carbon content. Also, the collection system becomes overheated within a short time due to the high volume of hot CO gas formed.

Concurrent with the studies to improve electrode strength and vaporization, the carbon purity versus oxide fume product purity was being investigated, particularly with regard to sulfur and SiO_2 . The existence of sulfur in the final product was somewhat surprising when considering the extremely high arc temperatures for it was thought that sulfur and any other similar elements would be removed by oxidation to a gaseous oxide by-product and not condense into the fume product, or at worst be diluted to the point of no concern. It was established, however, that sulfur does react quite readily with certain elements during condensation of the vapor; and the concentration in the product increases as the amount of carbon in the electrode is increased.

Dual approaches were studied for sulfur removal. One was to employ high purity materials, e. g. G-38 graphite. This led to reduction of sulfur levels in the product from 300-500 ppm to 30-70 ppm. However, the strengths of the electrode prepared with this graphite were very poor, and in several instances, the electrodes powdered during baking.

The other approach to sulfur removal was the calcination of the oxide fume product in air prior to reduction. A series of experiments revealed that calcining at 600°C for 4 hours in air effectively removed sulfur to less than 30 ppm.

Since stronger electrodes resulted when the higher sulfur bearing (.063%) carbon and binder were used, a series of electrodes was made using different carbons. (See Appendix A for analyses of carbons.) The sulfur contents of the fume products were all reduced to less than 30 ppm after calcination. Also from these experiments, it appeared that the electrodes prepared with Thermax carbon were the strongest.

Next, a series of runs was conducted using 40 and 50% Thermax carbon and 10% Black Pearl and 10%G-48 carbons in the electrode formulations to determine the effect of the SiO_2 ash content upon the SiO_2 content of the product fume. The 10% content was chosen to compensate for its higher sulfur content and to facilitate sulfur removal during subsequent calcination of the fume prior to reduction. Furthermore, the lower carbon would improve the yield per unit weight of electrode vaporized. Table 2 lists typical data from these studies.

TABLE 2

CHEMISTRIES OF ELECTRODES AND POWDERS
USING VARIOUS CARBONS

	52	58		62		64		
	Electrode	Reduced Powder	Electrode Powder	Reduced Powder	Electrode Powder	Reduced Powder		
Nickel	28.5	56.3	11.0	48.9	11.0	36.8	11.0	41.4
Cobalt	13.5	27.4	4.6	21.3	4.6	14.6	4.6	15.9
Molybdenum	24.0	5.4	35.7	10.8	35.7	18.0	35.7	19.3
Tungsten	24.0	4.4	38.7	10.2	38.7	16.6	38.7	14.5
Zirconia	10.0	2.1	10.0	2.3	10.0	7.9	10.0	6.0
Silica		~4		~5		.023		.015
Sulfur		<30ppm		<30ppm		<30ppm		<30ppm
Carbon	50% Thermax		40% Thermax		10% Black Pearl		10% G-48	

The sulfur contents of the fume product prior to calcination were 150-250 ppm, and were reduced by calcining in air for 4 hours at 600°C to less than 30 ppm, the limit of sensitivity of our analytical method.

The silica contents of the powders prepared from electrodes which contained Thermax carbon were exceptionally high. Although it was expected that the powder produced using Thermax would be higher in silica than those from the G-48 or Black Pearl carbons, a material balance considering the SiO₂ content of all the materials used could not account for more than 1% SiO₂ in the products of Runs 52 and 58. The source of the excess silica found has not been determined.

Vaporization of the electrodes containing the lower carbon contents was also improved. For the same electrode compositions, considerably more molybdenum, tungsten and zirconia were converted to fume product for the electrodes containing 10% carbon (Runs 62 and 64) than those containing 40 and 50% carbon (Runs 52 and 58). The over-all yield was also approximately doubled.

Since it is somewhat difficult to prepare electrodes using graphites (G-38 and G-48) due to their poor wetting characteristics with the binder, all subsequent electrode preparations were made using the Black Pearl carbon.

Several runs were made with minor variations in electrode chemistry to produce fume product for reduction, sintering and electron microscopic evaluation. Table 3 shows the electrode and reduced powder compositions. Runs 73 and 74 were made identical to illustrate the reproducibility of the process when all variables are held constant.

The high control of composition is reflected in Runs 72, 73, and 74 in Table 3. The electrode chemistry of Run 73 was modified slightly over 72 to compensate for the high molybdenum and tungsten and low cobalt in the product. Run 74 was prepared identically to 73. The chemical analyses of the two runs (73 and 74) are considered identical within the experimental error of the analytical methods used.

The spectrographic analysis of reduced powder from Run 74 indicates a silicon content slightly higher than that desired. The source of the silicon has not been determined and this problem will be studied carefully in future material preparations.

ELECTRODE AND PRODUCT ANALYSIS FROM ELECTRODES CONTAINING 10% BLACK PEARL

	66		67		71		72		73		74	
	E	P	E	P	E	P	E	P	E	P	E	P
Nickel	15.6	42.0	20.7	49.9	24.1	65.7	24.1	55.3	23.5	59.4	23.5	58.4
Cobalt	5.6	13.4	6.9	14.4	7.3	16.6	7.3	15.2	7.8	16.9	7.8	16.2
Molybdenum	40.4	16.5	37.4	12.5	37.4	6.4	37.4	11.5	36.2	9.0	36.2	9.5
Tungsten	34.9	22.7	32.0	20.2	29.0	8.6	29.0	14.4	27.7	9.8	27.7	10.5
ZrO ₂	3.5	3.0	3.0	2.7								
ThO ₂					2.2	1.3	2.5	2.0	4.9	2.6	4.9	2.7
Total Oxygen									1.08			1.17
										.01		.01
										.001		.003
										.01		.02
										.08		.08
										.015		.015
										.015		.015
										.3		.3

E = Metal equivalent of electrode
P = Reduced metal powder

by spectrographic analysis

E = Metal equivalent of electrode

P = Reduced metal powder

by spectrographic
analysis

2. Reduction of Submicron Oxide Fume

For the experimental reduction studies, powders are reduced in a 2" diameter Inconel tube which is externally heated by a resistance wound tube furnace. Approximately 15 grams of oxide fume in a molybdenum boat is heated in a hydrogen atmosphere to 800°C (approximately 1 hour to temperature) and held for 1 hour at temperature. The reduced powder is cooled in hydrogen for approximately 1 hour and the system flushed with argon. The powder is taken directly into the argon atmosphere drybox without exposure to the air. The Inconel tube is attached to the drybox, and is isolated from the drybox by an O-ring sealed, threaded cap which is secured from within the box.

Because of the very low bulk density of the oxide fume (approximately .13 gms/cc) considerable shrinkage takes place during reduction. The reduced powder bed consists of isolated, loosely sintered, agglomerates. The agglomerates are quite friable and readily crush to pass a 100 mesh screen. A typical screen analysis after crushing is

+100	.5%
-100 +200	5.5
-200 +325	36.0
-325	58.0

Under these reduction conditions the powder is not pyrophoric in air.

The reduction cycle in the large retort is ambient to 650°C in 15 hours, hold at 750°C for 3 hours (including the 15 minutes required to reach the 750°C temperature), then cool. The complete cycle is carried out under hydrogen at a flow rate of 50 cu ft/hr. After cooling, the retort is flushed with argon and the contents dumped into a sealed container also under argon. The container is then taken into the drybox and emptied. The powders produced under these reduction conditions are not pyrophoric in air either.

All powders used in the subsequent sintering and evaluation studies have been crushed to pass a 100 mesh screen. Some cursory examinations were made with minus 325 mesh powders for comparative purposes only.

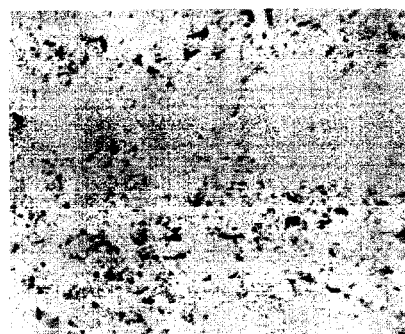
3. Sintering of Metal Powders

The evaluation of sintering characteristics was made on pellets 1/2" diameter by 1/4" thick. A few specimens 1" diameter by 1" long were made from lots reduced in the large retort where sufficient powder was available. All powders were precompacted in a die at a load sufficient to provide a pellet which could be handled. The pellet was wrapped in a one mil thick Teflon foil, bagged in a thin rubber tube, evacuated, and isostatically pressed at 25 tsi. All specimens for evaluation were pressed at this load since no significant differences could be observed in the density or microstructure of sintered pellets pressed at loads between 20 and 50 tsi and within the limits of the other variables investigated. The pressed specimens were then sintered in hydrogen for 3 hours at temperature, and some specimens were vacuum sintered for comparative purposes. Table 4 lists representative sintering data. It appears that in Runs 66 and 67 (ZrO_2 dispersion) a peak density is obtained at about 1250°C. A peak density was not observed in Runs 73 or 74 (ThO_2 dispersion). Typical metallographic structures are shown in Figure 12.

Surprisingly, it was not possible to reduce the sulfur levels to acceptable values using the previously determined 600°C calcination treatment. Calcining at 750°C for 12 hours was determined to be necessary for the reduction of sulfur to the 30 ppm level. This high temperature requirement caused some concern for the possible loss of molybdenum oxide through volatilization, but check analyses indicated that no molybdenum had been lost. The bulk density of the oxide fume, however, did increase to approximately twice that of the uncalcined material. Although no studies were made as to the effect this would have on the reduction cycle, no gross effects were noted.

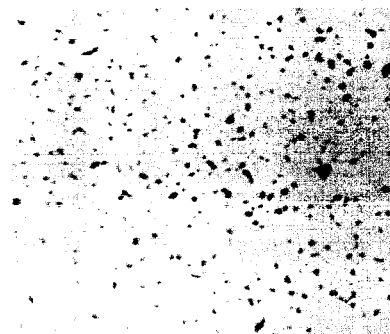
Figure 13 shows the microstructure observed on the sintered specimens of Run 74 having various sulfur levels. It is also noted in Table 4 that the densities of the higher sulfur bearing specimens are greater than those of the low sulfur bearing samples. It is conceivable that some liquid phase sintering occurred.

There does not appear to be a significant difference among the microstructures obtained by vacuum sintering and sintering in hydrogen, or any effect from presintering at a lower temperature, within the limits of the variables studied. From the data obtained, it appears that adequate densities can be obtained for subsequent working (extrusion) by sintering for 3 hours at 1250-1300°C in a hydrogen atmosphere.



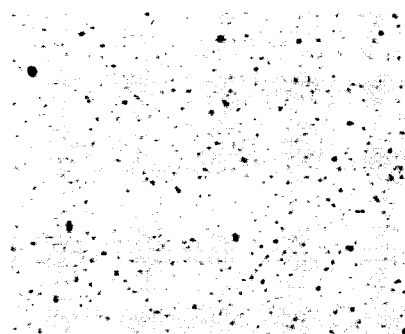
1000°C

250x



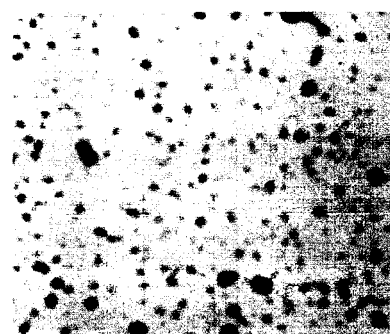
1200°C

250x



1300°C

250x



1350°C

250x

FIGURE 12

MICROSTRUCTURE OF POWDER FROM RUN 66
SINTERED FOR 3 HOURS IN HYDROGEN AT
VARIOUS TEMPERATURES. ZrO_2 DISPERSION

TABLE 4

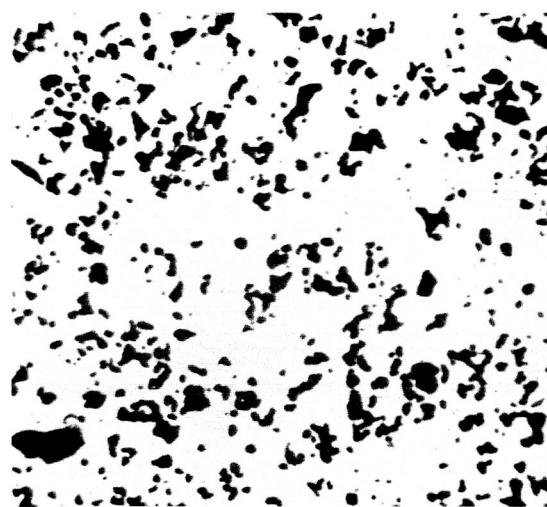
TYPICAL SINTERING DATA

Run No.	Sintering Conditions		Density	Remarks
66 ZrO ₂ dispersion	3 hrs. H ₂	1000°C	9.2 g/cc	All densities by water immersion. Theoretical density assumed in all cases to be 10 gms/cc.
		1100	9.0	
		1200	10.3	
		1250	10.1	
		1300	10.0	
		1350	9.6	
67 ZrO ₂ dispersion	3 hrs. H ₂	1000	9.1	Hardness R _C -18
		1100	9.6	
		1200	9.9	
		1250	10.0	Hardness R _C -24
		1300	9.8	Hardness R _C -22
		1350	9.8	
73 ThO ₂ dispersion	3 hrs. H ₂	1300	8.8	-325 mesh powder
			8.7	
	3 hrs. vac	1300	8.5	
74 ThO ₂ dispersion	3 hrs. H ₂	1300	9.4	Reduced powders from oxides calcined at 600°C 8 hrs. Residual sulfur content = 250 ppm
	8 hrs. H ₂	1300	9.4	
	2 hrs. H ₂	1000 -		
	3 hrs. H ₂	1300	9.4	
	2 hrs. H ₂	1000 -		
	3 hrs. H ₂	1300	9.4	
	2 hrs. H ₂	1000 -		
	3 hrs. H ₂	1300	9.4	
	2 hrs. H ₂	1000 -		
	3 hrs. vac	1300	9.4	
	3 hrs. H ₂	1300	9.2	Oxide calcined at 700°C S = 150 ppm.
	3 hrs. H ₂	1300	8.7	
	3 hrs. H ₂	1300	8.8	Oxide calcined at 750°C. Sulfur content less than 30 ppm.
	16 hrs. H ₂	1300	8.6	
	18 hrs. H ₂	1300	8.8	



150 ppm Sulfur

250x



<30 ppm Sulfur

250x

FIGURE 13
MICROSTRUCTURE OF POWDER FROM RUN 74
SINTERED FOR 3 HOURS IN HYDROGEN AT
1300°C. ThO₂ DISPERSION

A cursory examination was made of the microstructure of specimens sintered at higher temperatures. Figure 14 shows the microstructures obtained by sintering powders from Run 73 for 3 hours at 1425° and 1450°C. The 1450°C specimen was at temperature for 20 minutes when the compact began to melt. There does not appear to be any gross agglomeration or growth of the dispersion due to this incipient melting treatment.

4. Electron Microscopic Evaluation

4.a ZrO_2 Dispersion

Electron micrographs were made on specimens from Runs 66 and 69. Figures 15 and 16 show typical structures obtained from the ZrO_2 dispersion alloys. It is quite obvious that the submicron dispersoid particle size was not achieved in these runs using ZrO_2 . Although there are some small submicron particles, the majority of the dispersion is well in excess of the 0.1 micron average size desired. It appears that the larger particles are located at the grain boundary triple points. There also appears to be a considerable second phase in the grain boundaries themselves.

Other studies in this laboratory have revealed that ZrO_2 does not always vaporize readily in the high intensity arc to form discrete solid submicron particles, but that hollow balloons are sometimes formed. Needless to say, this was surprising since it is anomalous to all other oxide systems studied previously.

As a result of these findings no further studies were made using ZrO_2 as the dispersion.

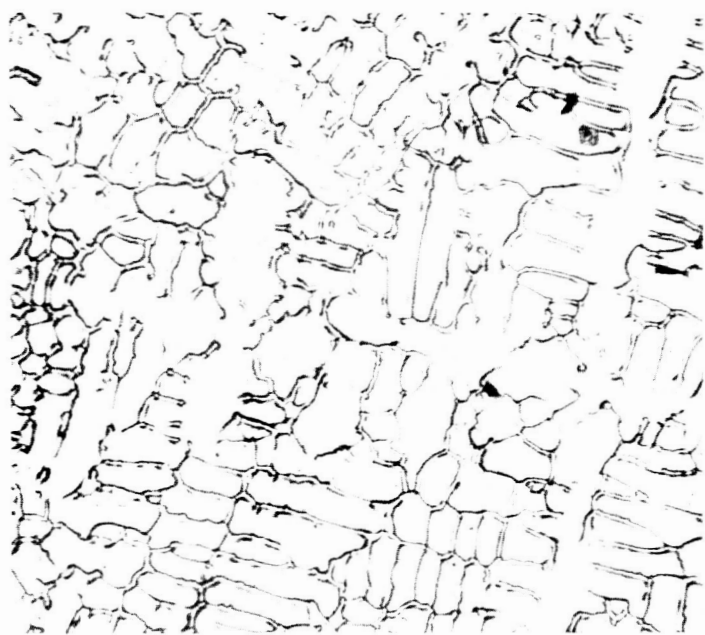
4.b ThO_2 Dispersion

Several runs were made in which ThO_2 was substituted for the ZrO_2 . Typical electron micrographs of specimens prepared from ThO_2 containing Runs 73 and 74 are shown in Figures 17 and 18. It is evident that the dispersion has been maintained in a submicron state with excellent uniformity. In Figure 18 it appears that there is some loose agglomeration of particles.



1425°C

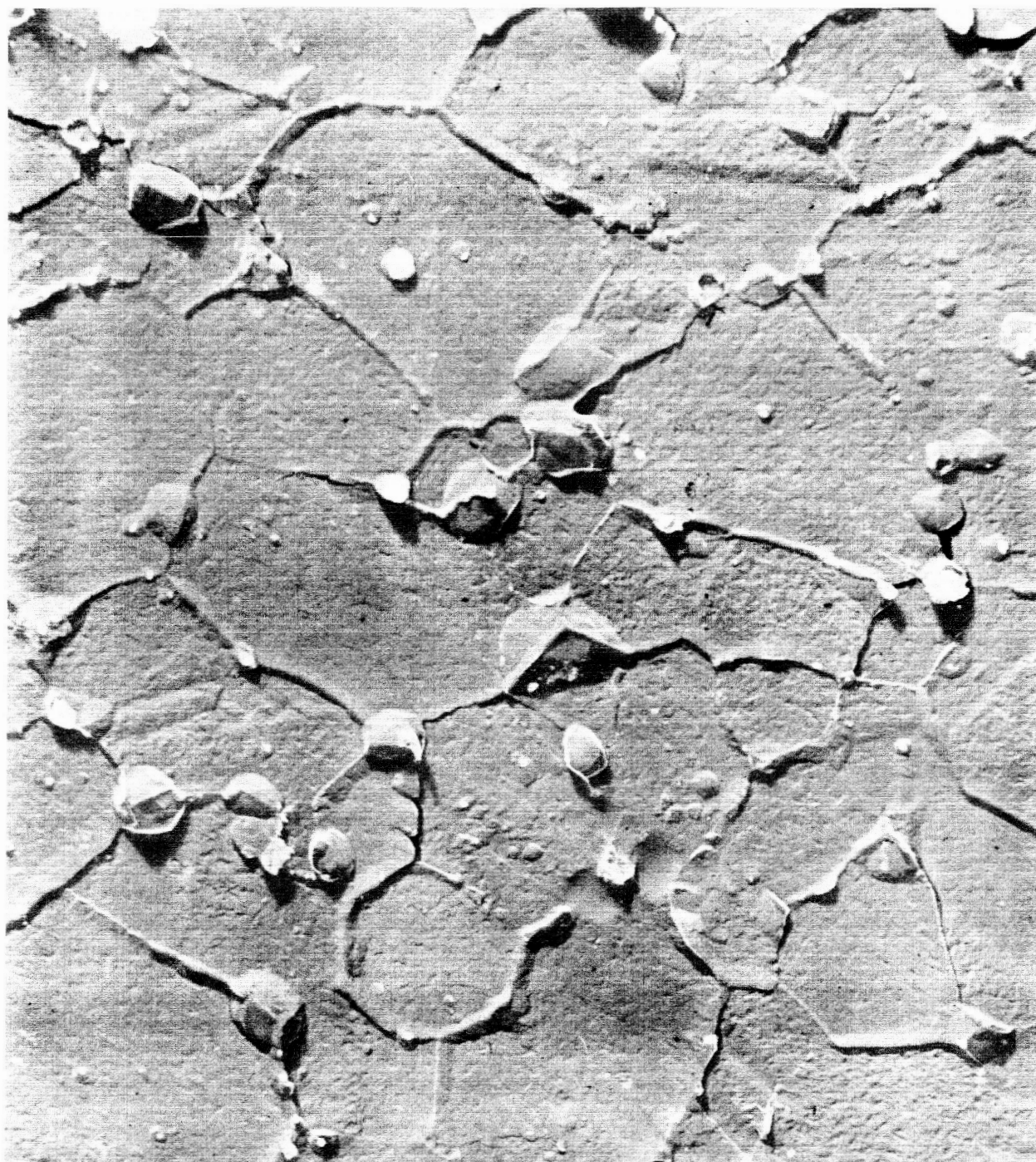
250X



1450°C (melted)

250X

FIGURE 14
MICROSTRUCTURES OF SPECIMENS (RUN 73)
SINTERED AT 1425 AND 1450°C



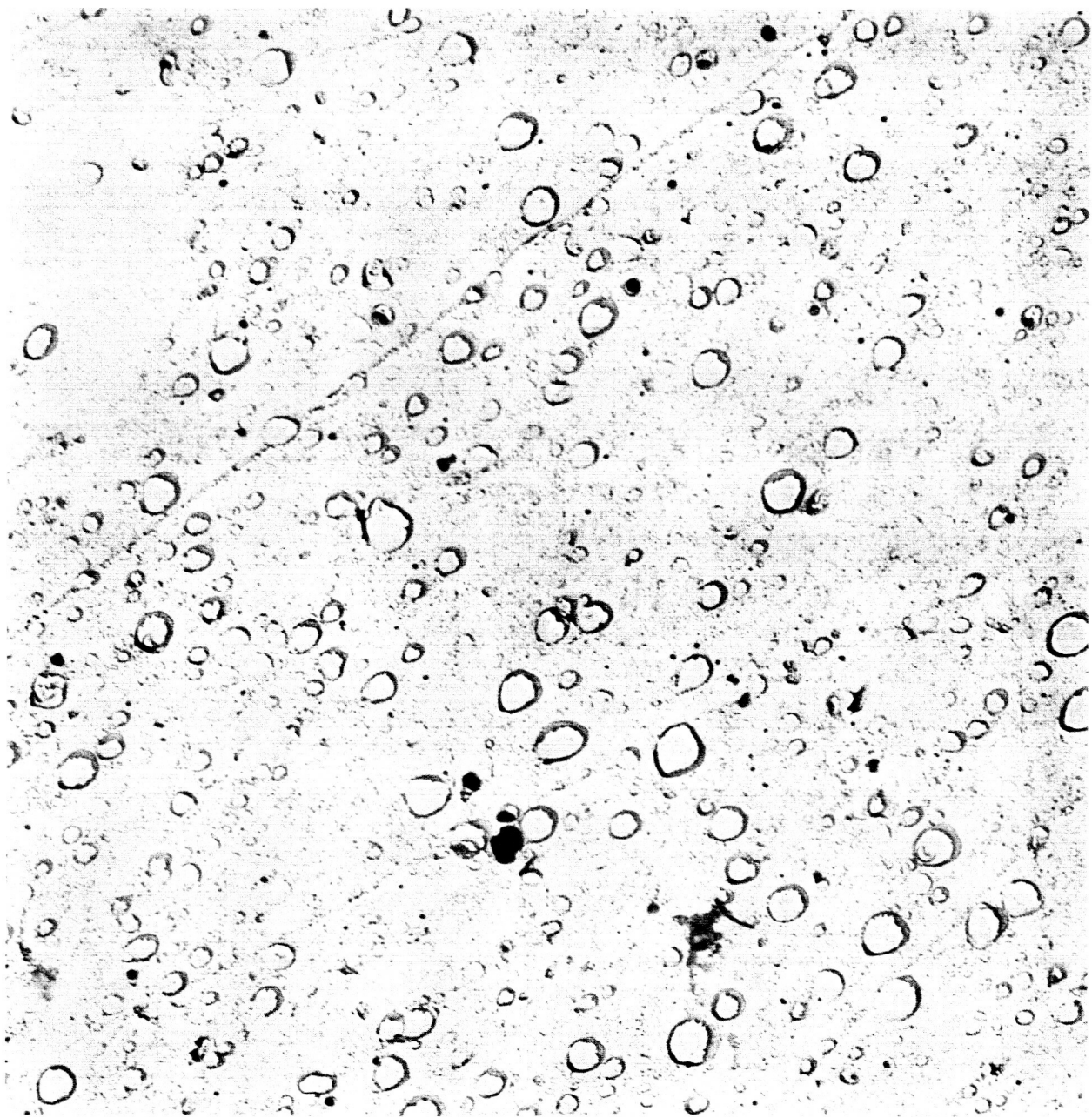
16,000X

FIGURE XV NICKEL ALLOY CONTAINING ZrO_2



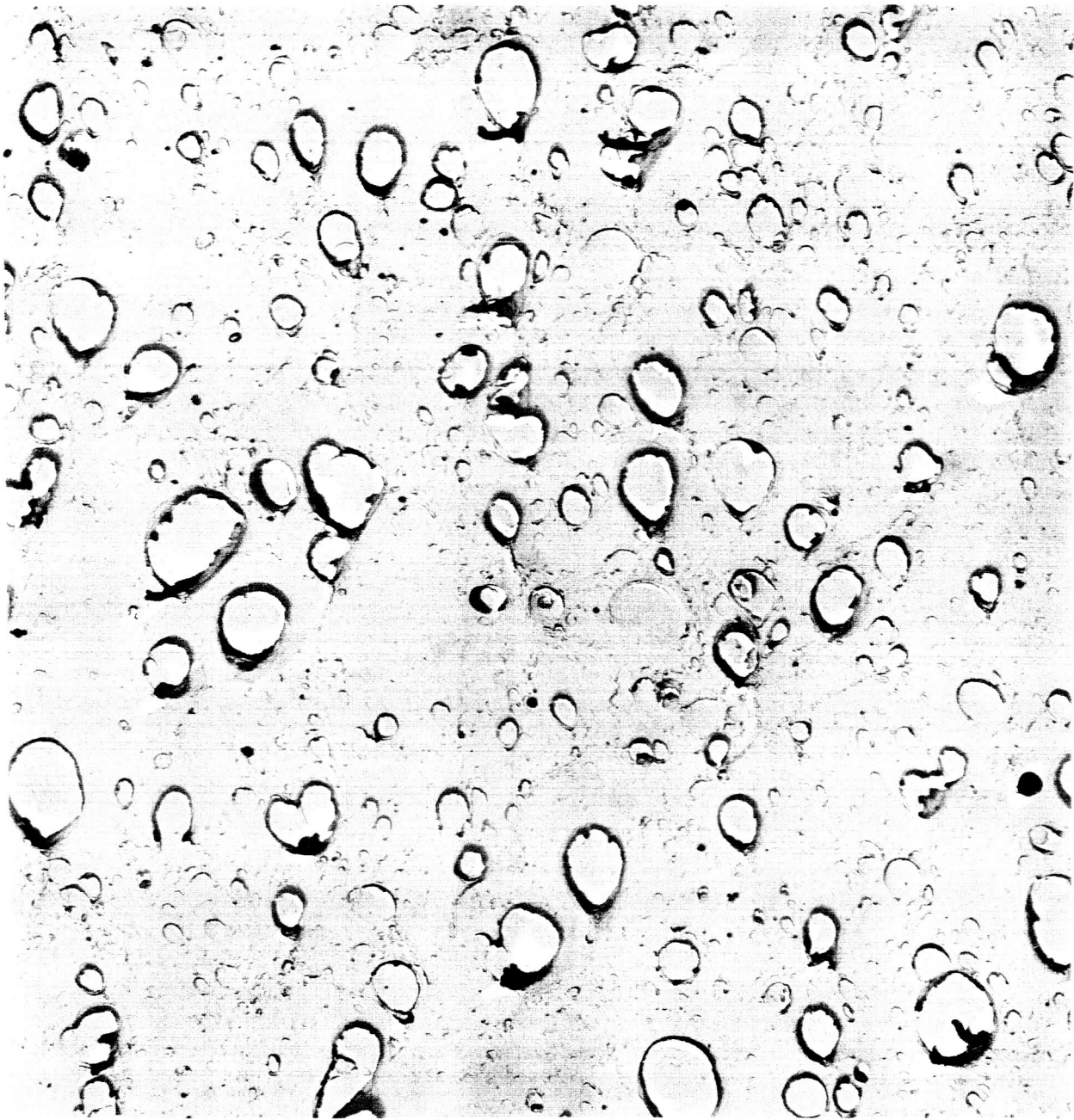
30,000X

FIGURE XVI NICKEL ALLOY CONTAINING ZrO_2



16,000X

FIGURE XVII NICKEL ALLOY CONTAINING ThO_2



30,000X

FIGURE XVIII NICKEL ALLOY CONTAINING ThO_2

Measurements by lineal analysis indicate the average particle size of Run 73 (Figure 17) to be 0.12 micron with an average interparticle spacing of 0.45 micron. The average particle size of Run 74 (Figure 18) was determined to be 0.05 micron with an average interparticle spacing of 0.2 micron. Approximately 300 particles were involved in each count.

APPENDIX A

RAW MATERIALS AND CHEMICAL ANALYSES

APPENDIX A

RAW MATERIALS AND CHEMICAL ANALYSES

Nickel Powder

Grade G-09

Sherritt Gordon Mines Limited

Fort Saskatchewan, Canada

Cobalt	0.090%
Copper	0.003
Iron	0.009
Sulfur	0.004
Phosphorus	<0.001
Carbon	0.023
H ₂ loss	0.46
Nickel	Balance

Cobalt Powder

300 Mesh

African Metals Corporation

New York, New York

Calcium	0.048%
Copper	0.001
Iron	0.063
Manganese	0.013
Nickel	0.085
Silicon	0.032
Sulfur	0.006
Carbon	0.021
H ₂ loss	0.209
Cobalt	Balance

Molybdenum Trioxide

Reagent

Matheson Company, Inc.

East Rutherford, New Jersey

Ammonium	0.002%
Chloride	0.002
Heavy Metals	0.005
Insolubles in NH_4OH	0.010
Nitrate	0.003
Arsenate, Phosphate and Silicate	0.0005
Sulfate	0.020
Assay	99.5

Tungstic Oxide

Yellow

Wah Chang Corporation

Glen Cove, New York

Aluminum	0.001
Calcium	0.001
Cobalt	0.001
Chromium	0.001
Copper	0.001
Iron	0.001
Magnesium	0.001
Manganese	0.001
Molybdenum	0.007
Nickel	0.001
Lead	0.001
Silicon	0.001
Tin	0.001

Zirconia

Reactor Grade-Micronized
Zirconium Corporation of America
Solon, Ohio

Aluminum	100 ppm
Boron	< 1
Cadmium	< 1
Calcium	700
Chlorine	12
Chromium	10
Cobalt	< 10
Copper	< 10
Fluorine	< 10
Hafnium	< 50
Iron	170
Lead	< 10
Magnesium	200
Manganese	< 10
Molybdenum	< 10
Nickel	< 10
Silicon	300
Sulfur (SO ₄)	480
Tin	< 10
Titanium	< 10
Vanadium	< 10
Loss on Ignition	100
ZrO ₂	Balance

Carbons

	Ash	SiO ₂	Sulfur	
Philblack E	0.17%	> 0.01	0.6%	(L)
G-38	0.18	0.18	< 10 ppm	(L)
G-48	0.019	< 0.01	< 30	
Black Pearl	0.019	< 0.01	800	
Thermax	0.16	0.14	70	(L)
Cathodes			30	(L)
Binder			630	(L)

(L) Analysis made by Ledoux and Company
 All others made by Vitro Laboratories